Synthesization, Characterization and Application of Nano-Particles Ferric Oxide in Sodium Sulfide Oxidation

By

Amira Rizwana Mohamed Yusoff
(6968)

A project dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

January 2009

Universiti Teknologi PETRONAS
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Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

.....

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ABSTRACT

Sulfides usually found in the wastewater produced by chemical and petrochemical industries such as tanneries, refineries, polymer industries. Removing sulfides from the wastewater is currently a big challenge to the industries because sulfides are soluble in water and various research and technologies have been studied and developed in order to remove sulfides content. In this project, the author is focusing on removing sulfides through oxidation process by using hydrogen peroxide as an oxidizing agent with the presence of nano-particles ferric oxide as a catalyst. Nano-materials are increasingly gaining the attention of the scientific community and also public due to their various applications in the industries for example as a catalyst. In this project, author will developed the procedure in preparing ferric oxide nano-particle as a catalyst and the application of it in sodium sulfide oxidation process. Basically three stages are involved, the synthesization, characterization and application. In application stage, the author will study two parameters of the oxidation rate that is catalyst loading and sulfide concentration. The effect of these parameters will be study by varying the variables for these parameters. The results shows that after the more catalyst added, the oxidation process increase by time and removal of sulfide can be achieve faster. The objectives for this project are to successfully produce nano-particle ferric oxide as catalyst and to apply it in the sulfide oxidation process.

ACKNOWLEDGMENT

I would like to take this opportunity to acknowledge and thank everyone that has given me all the supports and guidance throughout the whole period of completing the final year project. Firstly, many thanks to the university and the Final Year Project coordinators that have coordinated and made the necessary arrangements, especially in terms of the logistics, for this study.

I must also acknowledge the endless help and support received from my supervisors, Assc. Prof. Dr. Saikat Maitra (FYP II) and Prof. Binay K. Dutta (FYP I), during the whole period of completing this final year project. Their guidance and advices are very much appreciated. Apart from that, many thanks to Mr. Naveed Ahmad, with the guidance and helps for the completion of the experiments in the lab.

I would also like to thank the lab technicians in UTP, especially Pn. Azimah and Mr. Fazli for the supports given in terms of the preparation of logistics and lab schedule during the lab experiments for this study. Their continuous support and help throughout the whole period of experiments have been a great help to me and very much appreciated.

Finally, thanks to my fellow colleagues for their help and ideas throughout the completion of this study. Thank you all.

CHAPTER 1
INTRODUCTION

1.1 BACKGROUND STUDY

Sulfide removal from wastewater has been a great challenge in for the people in the industries due to the hazardous properties of it. Sulfide is produce when any organic or inorganic material contains sulfur degrade. Sulfide tends to convert into hydrogen sulfide which is hazardous to the life forms. Hydrogen sulfide is toxic, corrosive and gives bad odor (rotten egg smell) which is undesirable.

Many researches and studies have been done to remove sulfide content in the wastewater. One of the methods identified is oxidation process by using hydrogen peroxide as oxidizing agent. It has been proven that hydrogen peroxide can oxidize the sulfide to sulfate. But the process is quite slow comparing to other methods even though it can remove the sulfide content successfully.

So, several researches have been studied on adding catalyst in the oxidation process to see if they can improve the rate of oxidation. Nano-materials is currently is one of the most developed technologies. Due to its good performance, such as magnetism, catalysis, and gas-sensitivity and so on, they are widely applied in various fields. The use of nano-materials as catalyst in this oxidation process might improve the rate of sulfide oxidation tremendously. Usage of ferrous ion as catalyst in the oxidation process has been done. Synthesizing and characterized the nano-particles of ferric oxide to be used as a catalyst is done. With that, nano-particles ferric oxide as a catalyst in the oxidation process by using hydrogen peroxide, the effect is being is investigated.

1.2 PROBLEM STATEMENT

1.2.1 Problem Identification

Organic or inorganic sulfide is toxic and pollutants even in a low concentration to the toxic life forms. Sulfide in waste water can produce hydrogen sulfide which is highly toxic, corrosive and hazardous to human. Hydrogen sulfide gives a bad odor; rotten egg smell.

In waste water treatment plant, microbes purified the organic compound, biologically. Sulfides are produced if the microbes decay organic compound which contain sulfide. Sulfide ion can kill the microbes and lead to the hydrogen sulfide formation. So, it is necessary to remove or treat the sulfide. If there is enough dissolved oxygen, the sulfides can be re-converted to sulfates which are less hazardous than sulfides

Under Malaysian Regulations, Environmental Quality Act (Sewage and Industrial Effluent) 1978, Standard A and B, the sulfide concentration allowed on the final discharge are just 0.50 mg/L. In order to comply with the regulations, sulfide treatment is necessary in waste water treatment plant.

ENVIRONMENTAL QUALITY (SEWAGE AND INDUSTRIAL EFFLUENTS) REGULATIONS (1979) – STANDARD A AND B

(xviii) Boron	mg/l	1.0	4.0
(xix) Iron (Fe)	mg/l	1.0	5.0
(xx) Phenol	mg/l	0.001	1.0
(xxi) Free Chlorine	mg/l	1.0	2.0
(xxii) Sulphide	mg/l	0.50	0.50
(xxiii) Oil and Grease	mg/l	Not detectable	10.0

Figure 1: Standard A and B parameters limit

1.2.2 Significance of the project

This project has a great significance since now nano-materials are widely researched and applied in the industry. This technology is relatively new where and it is proven a better than technology at current.The physical and chemicals properties of nano-particles tends to be dependant on their size and shape or morphology. As a results, many scientist are focusing their efforts in developing simple and effective methods for fabricate nano-materials.

Synthesized and characterized nano-materials of controlled size and shape have a great potential in various applications including interconnects in electronic devices with super functions and bio-molecule separations; catalysis.

With the completion of this project, it is hoped to offer another opportunity window in nano-materials fabrication methods. Although there is a lot of studies and research on nano-materials preparation, it is hoped this project will bring better understanding in the potential of nano-particles ferric oxide. Further research on nano-particles ferric oxide are hoped to be done in future in order to expand more usage of it.

1.3 OBJECTIVES AND SCOPE OF STUDY

1.3.1 Objectives

The objectives of the study are:

- To synthesized, characterized and applied nano-particle ferric oxide as catalyst
- To study the potential of nano-particles ferric oxide as catalyst in the sulfide oxidation by hydrogen peroxide.
- To reduce sulfide concentration in wastewater.
- To study the effect of parameters; catalyst loading and sulfide concentration in the oxidation process.

1.3.2 Scope of Study

This study is aimed to cover the potential of hyperfine ferric oxide as a catalyst in the oxidation process. The study will be done in three stages that are synthesization, characterization and application.

In synthesization stage, this study aimed to develop the new method of preparing the ferric oxide by using different reactants that is urea, formaldehyde and ferric chloride.

In characterization stage, the study will cover the necessity to establish better understanding and control of the nano-particles synthesis and applications.

In the application stage, this study will cover the effect of variety of catalyst loading and sulfide concentration on the oxidation process. The effectiveness of ferric-oxide as a catalyst will also be study in this stage.

This study is not aimed to cover the information of preparing nano-particle ferric oxide and its application in industrial scale. The result of the effect of parameters is not for industrial scale. This study does not cover the effect of the catalyst on the other reaction of other components in the wastewater.

CHAPTER 2
LITERATURE REVIEW AND THEORY

2.1 REMOVAL OF SODIUM SULFIDE

Sulfides are generated when microbes decompose any organic material containing sulfur. Sulfides exist in waste water from oil refineries, paper and pulp mills and anaerobic sewage. Below is a chemical reaction, where hydrogen sulfide is formed as a by-product of anaerobic organic matter oxidation during bacterial sulphate reduction.

$$(CH_20)_{106}(NH_3)_{16}H_3PO_4 + 53SO_4^{-2} \rightarrow$$
$$53C0_2 + 53HC0_3^- + 53HS^- + 16NH_3 + 53H_2O + H_3PO_4$$

The generation of hydrogen sulfide in such systems is undesirable due to toxic and odorous nature of the gas in addition to the potential for corrosion following biological oxidation to sulphuric acid. Not only hydrogen sulfide is hazardous to human, it is also highly toxic to aquatic organism even at low concentration and has been cause of mass fish mortality in aquaculture systems.

2.1.1 Sources of Hydrogen Sulfide

Hydrogen sulfide is a gas formed by the decay of organic matter such as plant material. It is most commonly found in groundwater characterized by relatively low concentrations of dissolved oxygen and by a pH less than 6.0 (relatively acidic). In higher pH waters other forms of sulfur may be present (sulfide or bisulfide). Surface waters are typically less likely to contain hydrogen sulfide since flowing waters are aerated naturally, which promotes an oxidation reaction. The hydrogen sulfide either escapes as a gas or is precipitated as a solid.

Harmless sulfur bacteria are also found in many private water supplies and distribution systems. These bacteria feed off natural sulfur compounds in water, producing hydrogen sulfide as a result. Sulfur bacteria are not a risk to human health, but their presence in drinking water can be a source of unpleasant tastes and odors.

Sometimes hydrogen sulfide may only be present in the household hot water. This condition is caused by a biochemical reaction between sulfates in the water, sulfate-reducing bacteria, a magnesium rod in the hot water heater or organic matter in the water. If the odor problem in the water heater is caused by heat-loving sulphate-reducing bacteria, disinfect the water heater with chlorine bleach or hydrogen peroxide. Sometimes the reaction with the magnesium rod is the cause of odor problems. The purpose of the magnesium rod is to prevent corrosion of the water heater. Removing the magnesium rod will often prevent the odor problem, but will void the warranty and lead to the possible earlier deterioration of the tank. If corrosion is a concern, the magnesium rod can be replaced with a zinc or aluminum rod.

2.1.2 Sulfides treatment in waste water

Various technologies have been identified for the removal of the sulfides. It can be divided into the two main groups. That is vapor phase technologies and liquid phase technologies. Vapor phase technologies ventilate the point sources of odor problems. This technology is used for the air treatment and waste waters both treatments. This is the example of technologies working on the principle based on vapor phase technologies

- Wet scrubbing
- Liquid redox technology
- Biofiltration
- Scavengers
- Carbon adsorption.

Liquid phase technologies involve the treatment of a waste water stream to control the release of odor and corrosion causing compounds from the stream. Most liquid phase technologies involve the addition of a chemical to the waste water to either control the formation of odorous compounds or react with those compounds once they are formed. Liquid phase treatment not only controls the odor, but it provides corrosion control in addition to odor control. These are the example of technologies working on liquid phase technologies:

- Iron salts
- Bioxide process
- Anthraquinone
- Oxidizing agents.

In this project we are only focusing on oxidation process where we used hydrogen peroxide as oxidizing agent. Oxidation for waste water odor control involves the application of a strong chemical oxidizing agent to the waste water. The oxidizing agent is used to chemically react with dissolved sulfides, converting it to sulfate or sulfur.

The common oxidizing agents are hydrogen peroxide, ozone, permanganate, air and hypochlorite. Air is the naturally available oxidant .It is mostly used as an oxidant with a catalyst. Coal flash has been used as a catalyst in the oxidation of aqueous sodium sulfide in the temperature range of 303 to 333k.

One method of sodium sulfide removal from the wastewater is treating sodium sulfide with hydrogen peroxide at high ph in the presence of ferrous ion. This process is carried out at ambient temperature. In this process different reaction condition were applied. Five different concentrations of hydrogen peroxide were applied (0.25ml/L, 1.5ml/L, 1ml/L, 1.5ml/L and 2.5ml/L). Samples were collected during reaction at 30, 60, 90, 120, 150 180 min time intervals after hydrogen peroxide addition.

In this oxidation process the main product is sulfate. At a ph equal to 8.62 sulfide and sulfites present in the wastewater are converted into the sulfates according to the reactions below.

$$S^{-2} + 4H_2O_2 \rightarrow SO4^{-2} + 4H_2O$$

$$SO_3^{-2} + H_2O_2 \rightarrow SO_4^{-2} + H_2O$$

$$HSO_3^{-2} + H_2O_2 \rightarrow HSO_4^{-} + H_2O$$

During this process subsequent decline in the ph was also observed. The use of ferrous ion with hydrogen peroxide produces FeS, which is insoluble. But during this process smelling agents like hydrogen sulfide are also produce. During this reaction ferrous ion converts into the ferric ion. Ferric ion can remove sulfide by oxidizing it into the elemental sulfur while being reduce itself to the ferrous ion, which produces FeS.

The addition of ferrous ion does not have a significant effect on the odor control. Ferric ion is oxidized by auto oxidation and results formation of elemental colloidal sulfur. Reactions of ferrous ion oxidation to ferric ion and formation of FeS and colloidal elemental sulfur are given below:

$$Fe^{+2} + HS^{-} \rightarrow Fes + H^{+}$$
$$2Fe^{+3} + HS^{-} \rightarrow 2Fe^{+2} + S^{\circ} + H^{+}$$

Another method of removal of sodium sulfide from wastewater is treating the wastewater with hydrogen peroxide at freezing point. The reaction was found to be accelerated by freezing. The reaction rate at freezing point was found five times faster than at 25C°.

2.2 PREPARATION OF NANO-PARTICLES FERRIC OXIDE

The synthesis and characterization of nano-structured materials are the subject of intense current research. Hyperfine Fe_20_3 particle with good performance, such as magnetism, catalysis, gas-sensitivity and so on, are widely applied in various fields. It is highly significant to research and develop the methods for synthesis of nanometer)'-Fe_20_3.

With the development of nano-science and nanotechnology, the methods for preparation of Fe_20_3 have been greatly progressed; for example, laser vaporizing, micro-emulsion, co-precipitation and etc. However, there are such drawbacks as process complication, valued cost, and rigorous operation and so on in these methods.

The synthesis methods such as spray pyrolysis, precipitation, sol-gel, hydrothermal and combustion synthesis have been done to synthesis nano-particles. By altering the synthesis methods, the range of different nano-particles can be created. These synthesized nano-materials varied from uniformly sized spherical, nano-wires or nano-rods.

After the synthesization, the material is characterized to determine the size particle, crystal structure, composition, morphology, surface area and etc. Some of the equipments that are used for the characterization are XRF, SEM, XRD, FTIR, TGA, DSC and BET.

Studies revealed that gel-combustion method is the highly suited method for synthesizing nano-particles with high purity, stable meta-phases and in varying nano-particles size and shape by using relative simple equipments.

Sol-gel method is a liquid phase reaction that involves the polymerization of molecules in solutions, which results of solidification of solution to a gel. The state which fine particle is forms (1-200nm in diameter) are dispersed in liquid forms called colloids. When the colloids are sufficiently fluid and stable for a long period of time, the

colloids is called sol. Rigid solid formed by the evaporation of solvent from a sol is called gel. A gel is a semi rigid colloidal dispersion of solid particles in liquid. Typically the rigidity of the gel is such that it will not flow under the influence of gravity. Sol-gel processing can be done at room temperature which involves the dispersion of nano-particles in gel.

Other method is spray pyrolysis. Thin films are formed on heated substrates by spraying aqueous solution of metal compounds such as halides.

Precipitation method is when aqueous solutions of various salts react and compounds with low solubility precipitate out of the solution. By using various salts and controlling parameters such as temperature, it is possible to control the particle size of the nano-particles formed. This method suited for the production of fine particles.

Hydrothermal method is a method of synthesis of nano-materials from high temperature aqueous solutions at high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called autoclave, in which a nutrient is supplied along with water. Gradient of temperature maintained at the opposite end so the hotter end dissolves the nutrient and cooler end causes the seed to take additional growth. Examples of compounds can be synthesized using this method is simple and complex oxides, carbonates, silicates and etc. But, this method have some disadvantages, it need an expensive autoclaves, good quality seeds of fair size and its impossible to observe the crystal growth.

CHAPTER 3
METHODOLOGY

3.1 PROCEDURE IDENTIFICATIONS

3.1.1 Project Methodology

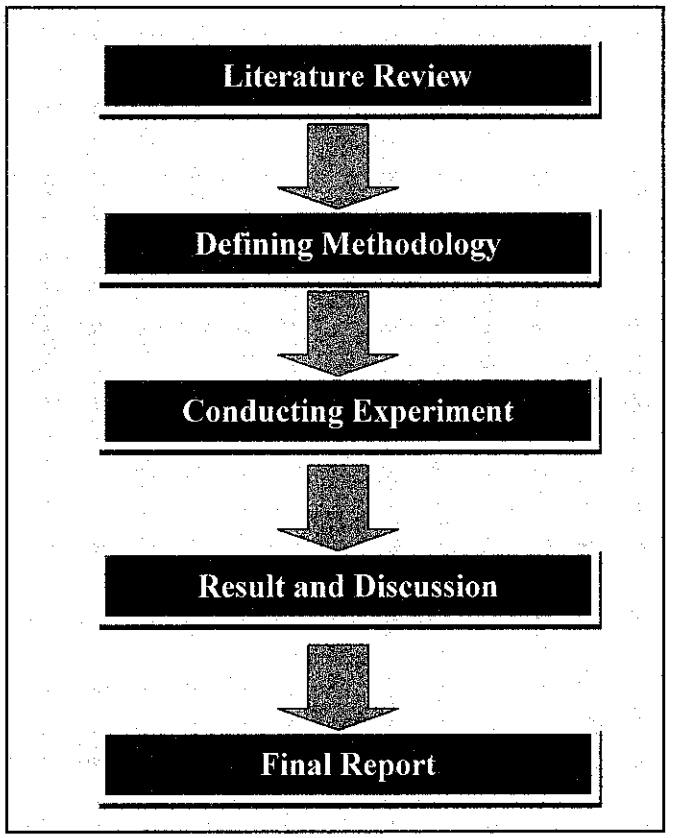


Figure 2: Project Methodology

The first step is to do the research on literature review and get more understanding on the project topic itself. Many researches have been done by a lot of people who have similar topics and objective with the project objective. Research was done by reading journals, articles, books and search on the Internet.

Based on the journals, articles and information gather, the methodology of the experiment is defined and developed. The methodology was discussed with supervisor to make sure it is the correct procedure.

Then, experiment can be conducted. This is the crucial stage for this project. Experiments done might not give correct results or output. The experiment might have to be done again and again until the correct output or results obtained according to theory. All experiments are done in UTP Laboratory. The results obtained are then discussed and analyze with the supervisor.

The last step is final report preparation. After all discussion and analysis done, the result and discussion are to be document as final report or dissertation. Dissertation is then submitted to supervisor and FYP coordinators.

3.1.2 Experiment Methodology

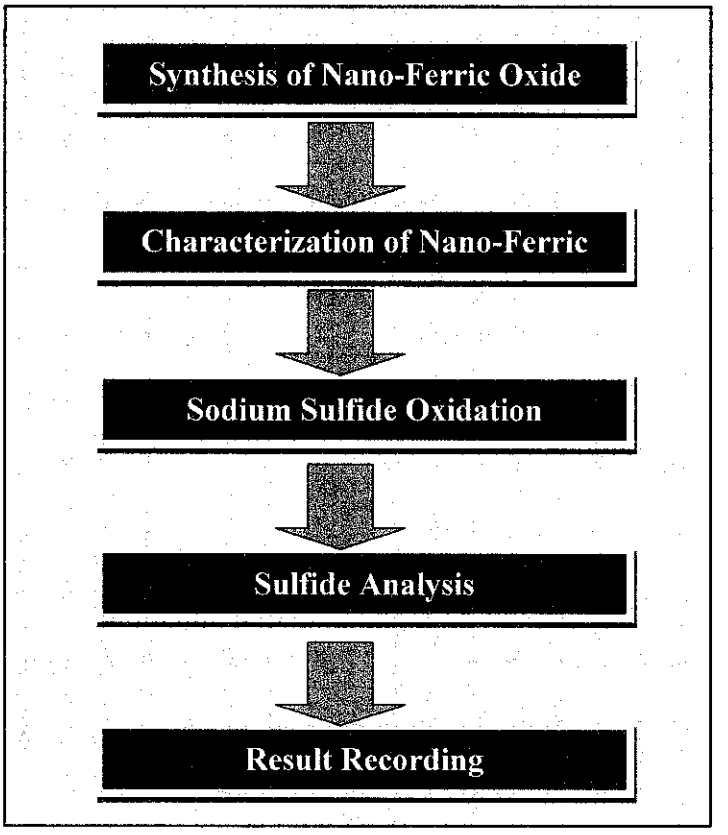
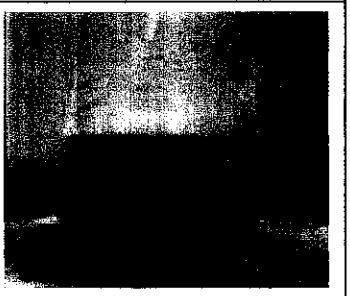


Figure 3: Experiment Methodology

3.1.2.1 Synthesization of Nano-particles Ferric Oxide.

STEP	DEFINITION	PICTURE
1	Reactants Preparation Ratio: Urea + Formaldehyde (1) + (4) - Total Mass of both should be 25g	
2	Preparation Ferric Chloride Fe_2cl_3 - 200mL of 2.5% Fe_2cl_3 solution.	
3	Aging - Both reactants are mixed and left for aging process 24 hours.	
4	Heating - The solution is heated to evaporate most of the water contents.	

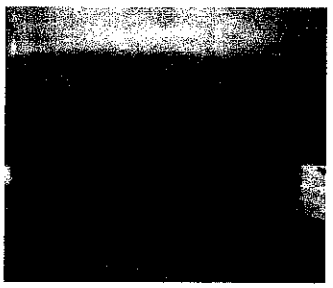
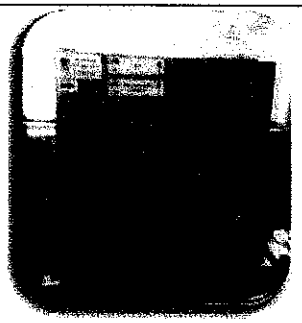
5	Resin and Gel Formation - During the heating resin and gel formation will occur.	
6	Drying - The left from the heating will be dried in over overnight - Then, the sample are burn for 1 hour under 800°C in the furnace	

Figure 4: Steps of synthesization of nano-particles ferric oxide

a) ***Reactions Preparation***

Ratio: Urea + Formaldehyde

(1) + (4)

- Total Mass of both should be 25g

Molecular Weight: 1) Urea = 60.07

2) Formaldehyde: 30.0262

1 mole of Urea + 4 moles of formaldehyde

We take 8.375 g of Urea; hence

8.375 g / 60.07 = 0.139 moles

Formaldehyde;

4 x 0.139 moles = 0.558 moles

Mass of formaldehyde: = 0.558 moles x 30.0262

= 16.75 g

Total Mass: 8.375 g + 16.75 g = **25.128 g ≈ 25 g**

Formaldehyde; 1.09 kg= 1L

25 = 15.36 mL ≈ **15.5 mL**

b) Preparation of Ferric Chloride Solution

The solution is mixed with 200mL of 2.5% Fe_2cl_3 solution 2.5%

= 2.5/100

= 0.025 M

Molecular Weight of Fe_2cl_3 = 162.21

Mass of Fe_2cl_3 = 0.025 x 162.21

= 4.055 g/L

If the solution needed is only 500 mL, then;

= 4.055 g/L x 0.5

= 2.027 g/ 500 mL

To make a 2.5% solution of ferric chloride, take 500 mL of distilled water and add 2.027 g of ferric chloride solid.

c) Aging

- The reactants mixed are kept for 24 hours for aging purpose.
- pH of the solution are measured to make sure it is at 8.5

d) Heating

After aging process, the solution is heated in fume hood cupboard at 110°C to evaporate most of water contents. The temperature is measured and controlled to be at 110°C to make sure only water content will evaporate during this heating process.

e) Resin and Gel Formation

During the heating process, the resin formation will occur and followed by gel formation. After the heating process, the solution will be colloids and slurry.

f) Drying

After the heating process, the left will be dried in oven for overnight at 110°C to completely remove the water content. Then, we will take the sample and burn it in the furnace for 1 hour at 800°C.This burning process is to remove the excess reactants, that is formaldehyde and urea mixed solution, and ferric chloride.

3.1.2.2 Characterization of Nano-Particles Ferric Oxide

In the characterization stage, we will used three equipment to analyze the ferric oxide synthesize. That is SEM, FTIR and XRD. The SEM (scanned electron microscopy) analyze is a common technique to determine the size of the particles. Since we are expecting hyperfine particles, the range is to be from 1- 200nm. Also, we are to analyze the surface area and crystal structure of the particles.

FTIR (Fourier Transform Infrared Spectroscopy) analyze is done to analyze bond in the sample. We will determine the type of the bond in the sample by the stretching frequency obtained from the analysis. XRD analysis is also done.

3.1.2.3 Application of Nano-Particles Ferric Oxide.

The ferric oxide obtained will be used as catalyst for the sulfide oxidation process. We used hydrogen peroxide as the oxidizing agent. Even without catalyst, the oxidation process will occur but by adding catalyst, we are to determine the effect on the oxidation process. Initially, there were four parameters to be study. That is catalyst loading, sulfide concentration, hydrogen peroxide dosage and temperature. But, due to time constraint only two parameters will be investigate; catalyst loading and sulfide concentration.

For catalyst loading, we will vary the loading from 0g, 0.25 g and 0.5 g. For sulfide concentration, we will vary the concentration from 600 ppm, 800 ppm and 1000 ppm. All experiment is done in the lab by using synthetic wastewater (sodium sulfide solution).

10mL of sample is taken at interval of 10 minutes for 1 hour. The samples are placed in test tube. The sample then is diluted with distilled water by ratio 1:100 because the limitation in the spectrophotometer .It can't read samples with high concentration. By diluting it, we will have a lower concentration reading.

Then, we will multiply the reading with the factor, in the case are 100. To get the reading, we have to use sulfide reagent 1 and 2. If there are any sulfides, the solution will turn blue after adding the reagents. Then, the sulfide concentration in the samples can be read by using spectrophotometer. A standard calibration curve has been done earlier and stored in the computer to get the reading.

To prepare sodium sulfide solution, we use hydrated sodium sulfide and diluted it in the distilled water. 1g of sodium sulfide diluted in 1L of distilled water will give 1L of 600 ppm sodium sulfide solution.

To get 800 ppm and 1000 ppm, we have to:

$$\frac{800}{600} = \frac{X_1}{1\text{g}} \quad ; \quad \frac{1000}{600} = \frac{X_2}{1\text{g}},$$

$$= \mathbf{1.333\ g} \qquad = \mathbf{1.667\ g}$$

So, to get 800 ppm solution we dilute 1.333 g of sodium sulfide in 1 L of distilled water. The same goes for 1000 ppm, where we diluted 1.667 g of sodium sulfide into 1 L of distilled water.

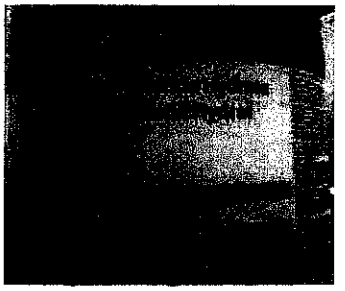


Figure 5: Sodium Sulfide Hydrated.

3.2 TOOLS

The equipments and tools use during the experiments period are:

- UV/Visible Spectrophotometer
- SEM (Scanned Electron Microscopy)
- FTIR (Fourier transform Infrared Spectroscopy
- XRD

CHAPTER 4
RESULT AND DISCUSSION

The experiments were repeated few times due to the incorrect results and output gained. For each stage, all results will be included in this report and the errors faced will be discussed.

4.1 SYNTHESIZATION OF NANO-PARTICLES FERRIC OXIDE

After heating process

Sample 1 Sample 2

Figure 6: Sample after the heating process.

In sample 1, during the heating process, the solution was not stirred and heated quite fast. We can see the excess reactants clearly; (*in white: excess urea and formaldehyde solution)* and the colloids not uniformly formed.

In Sample 2, we stirred the solution during the heating process. The colloids formed uniformly.

After drying process

Sample 1 Sample 2

Figure 7: Sample after the overnight drying in the oven

As, we can see after the heating process, gel formation occurred and the solid is produced. The sample after the heating process is more to brownish while the sample after the drying process (oven) is more to yellowish. In both sample, we can see some whitish component. It is the excess reactants which is urea and formaldehyde mixture which did not react with ferric chloride. This excess reactant will be burn out when drying the sample in the furnace.

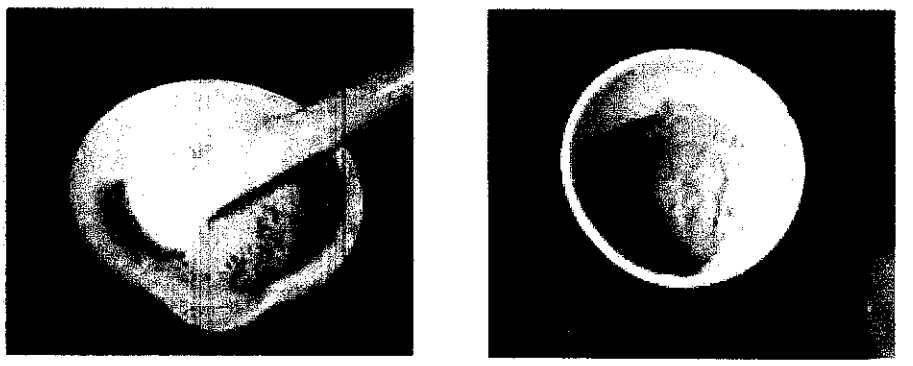
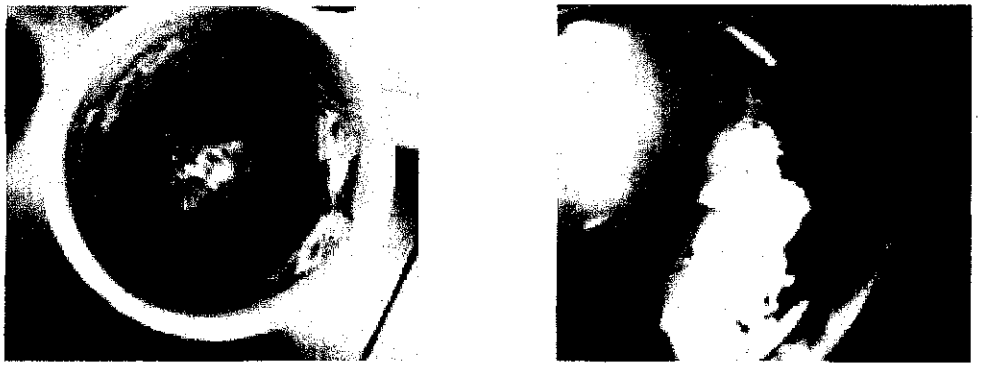


Figure 8: Preparation of sample before burning in the furnace.



Sample 1 Sample 2

Figure 9: Sample after the burning

For sample 1, the sample from the furnace is all burn out. This is due to a mistake or error done in the methodology. We used porcelain as the container of the sample because only porcelain can stand in the furnace. During the burning process, the lid should be left open for oxygen supply, but instead the lid was put on top covering the porcelain .The combustion was incomplete.

The error was taken into account and the process was repeated by using another sample. After the combustion, the left of the sample were dark maroon which is ferric oxide. Then the sample is sent for characterization.

4.2 CHARACTERIZATION OF NANO-PARTICLES FERRIC OXIDE

4.2.1 SEM Analysis

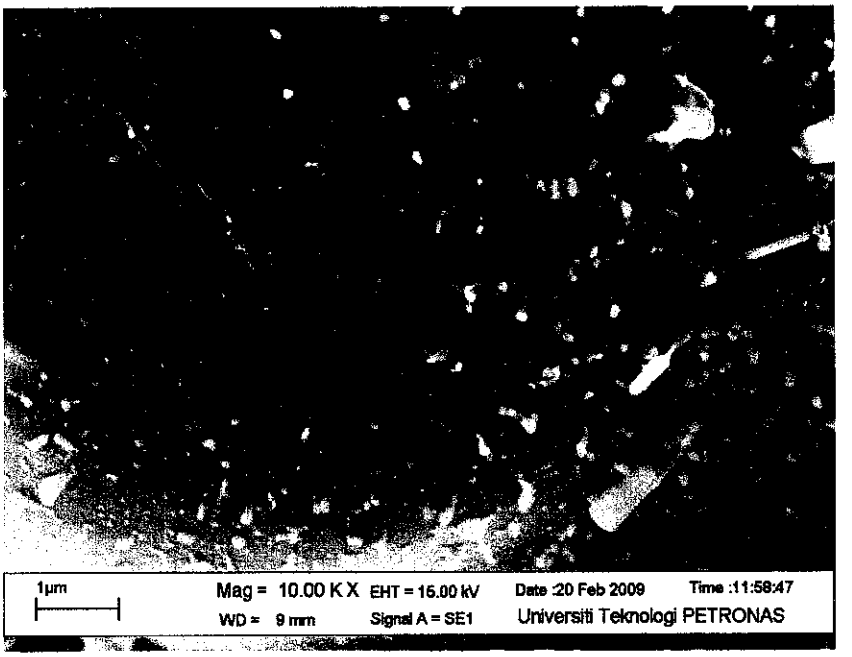


Figure 10: SEM Analysis for sample 1

Sample 1 was also send for SEM Analysis despite the condition of the sample after the burning process. No particles found and because the sample were all burn out. No size can be determined from this analysis. The experiment was repeated again.

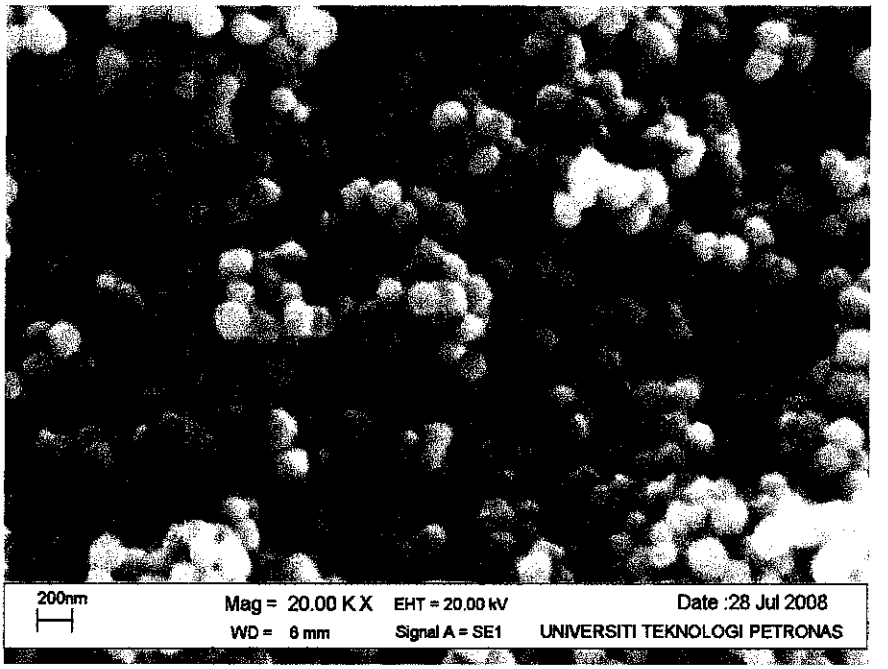


Figure 12: SEM Analysis result

This is the expected result for nano-particles size. We can see that the particles are in spherical shape and in the range of 200nm (the acceptable range is 1-200nm).

4.2.2 FTIR Analysis

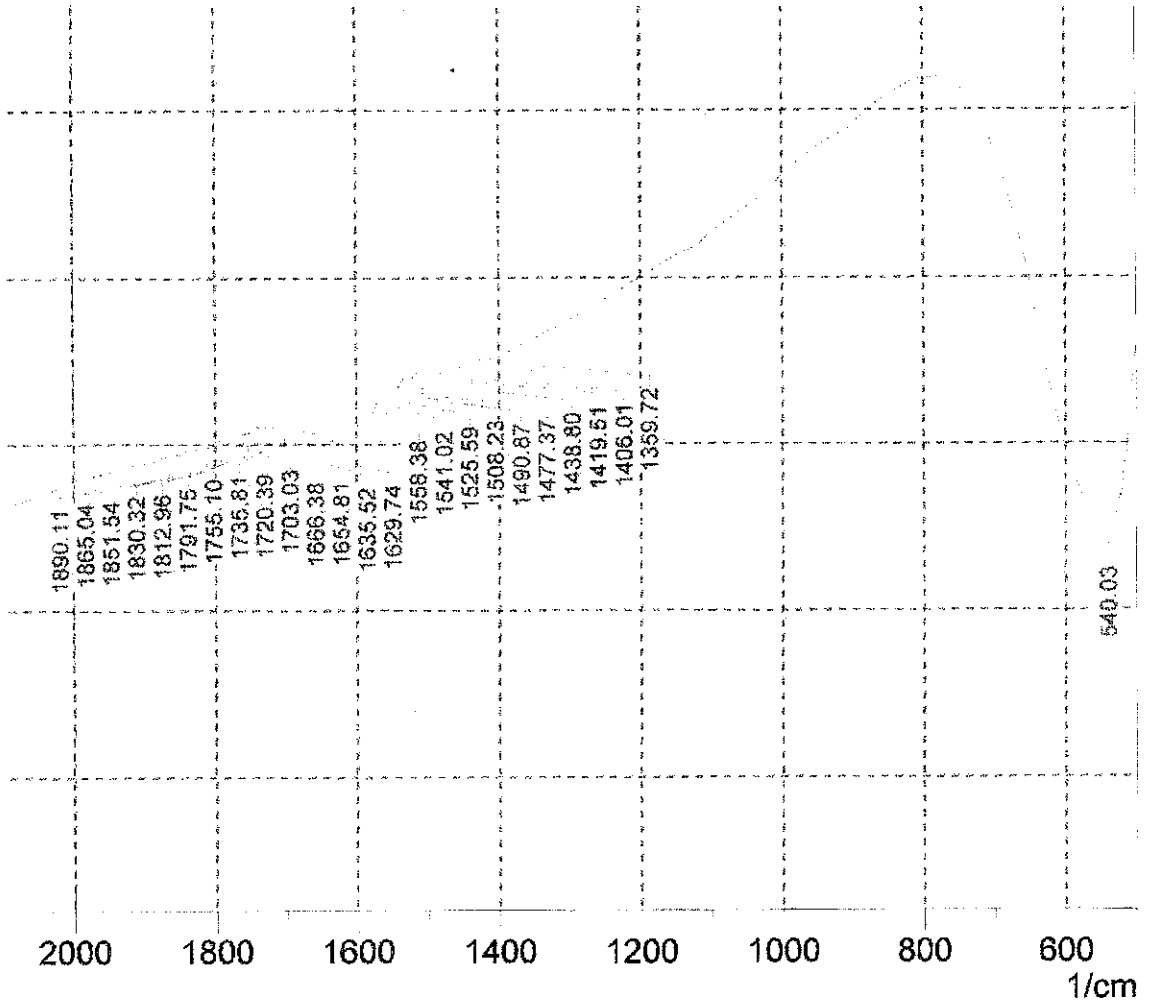


Figure 13: FTIR Analysis

In the FTIR spectra of the catalyst sample, no stretching frequency of free water is recorded (3600cm^{-1}) or bonded water (3400cm^{-1}). Bending vibrations from 1703.03cm^{-1} until 1558.38 cm^{-1} is due to inner lying OH- ions in the sample. Band at 540.03cm^{-1} is due to the Fe-O stretching vibrations

The materials contain traces of isolated Fe-OH and no free water. The cationic field of Fe was significant possibly because more polarizing Fe3+ ions as the bending vibration of OH- split into two planes. This sample can be called hydrated ferric oxide .

4.3 APPLICATION OF NANO-PARTICLES FERRIC OXIDE AS A CATALYST IN SULFIDE OXIDATION PROCESS.

4.3.1 The effect of catalyst loading on sulfide oxidation process.

In this experiment, we vary the catalyst loading (0g, 0.25g and 0.5g) to study the effects. First of all 1 liter of 600 ppm sodium sulfide solution is prepared. Then 2.6 mL of H_2O_2 added in the solution. The stated value above for the catalyst is added simultaneously with hydrogen peroxide and the experiment is run for 1 hour. At interval of 10 min, sample were taken, temperature and dissolved oxygen are recorded.

Experiment 1

Initial concentration = 600 ppm

Initial temperature = 26.4°C

Catalyst Loading = 0 g

Time (min)	Sulfide concentration (ppm)	Temperature (°C)	Dissolved oxygen (mg/L)
10	527	26.2	2.25
20	463	26.3	2.53
30	401	26.3	2.47
40	378	26.4	2.68
50	337	26.3	2.78
60	301	26.3	2.54

Table 1: Data recorded for catalyst loading of 0.00 g

Experiment 2

Initial concentration = 600 ppm

Initial temperature = 25.6°C

Catalyst Loading = 0.25 g

Time (min)	Sulfide concentration (ppm)	Temperature (°C)	Dissolved oxygen (mg/L)
10	486	25.6	1.86
20	425	25.3	1.57
30	387	25.4	1.78
40	341	25.4	1.96
50	301	25.5	2.04
60	265	25.7	1.83

Table 2: Data recorded for catalyst loading 0.25 g

Experiment 3

Initial concentration = 600 ppm

Initial temperature = 26.3°C

Catalyst Loading = 0.5 g

Time (min)	Sulfide concentration (ppm)	Temperature (°C)	Dissolved oxygen (mg/L)
10	386	26.3	2.78
20	378	26.3	2.65
30	338	26.4	2.44
40	306	26.4	2.78
50	267	26.5	2.73
60	105	26.5	2.64

Table 3: Data recorded for catalyst loading of 0.50 g

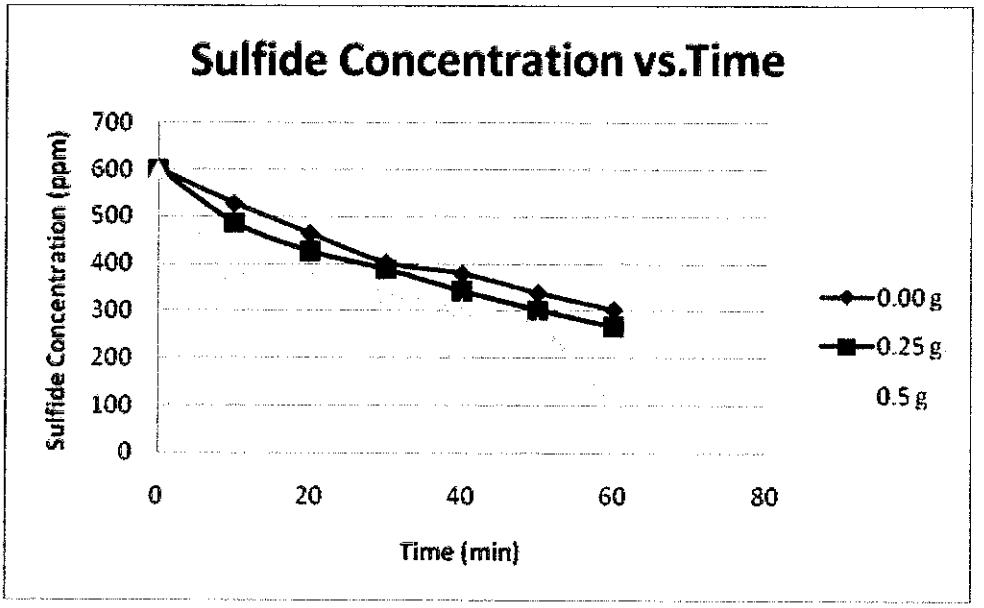


Figure 14: Sulfide Concentration vs. Time for different catalyst loading parameter

From the graph and data recorded, we can see that the time taken to remove the sulfide concentration decrease as we increase the catalyst loading. After 1 hour, the concentration left is 105 ppm for 0.5 g catalyst, 265 ppm for 0.25 g catalyst and 301 ppm for no catalyst added. The temperature does not change much during the process because the experiment was done in the room temperature. No external heat was supply during the process. The temperature does not play any role in the process for this experiment.

For dissolved oxygen, the more dissolved oxygen in solution, more sulfides can be converted to sulfate. If we see the difference in the data collected for catalyst 0.25 g and 0 g are not much. But if we see the dissolved oxygen recorded, experiment 2 recorded less dissolved oxygen than experiment 1. So, experiment 2 will has fewer sulfides convert to sulfate even though the load of the catalyst has increased. This explains the small difference in the sulfides concentration at the end of the experiment for experiment 1 and 2. So, we can conclude the more catalyst load in the oxidation process, the less time taken to remove the sulfide or complete removal.

4.3.2 The effect of sulfide concentration on sulfide oxidation process.

In this experiment, we vary the sulfide concentration (600 ppm, 800 ppm and 1000 ppm) to study the effects. First of the stated value of concentration of sodium sulfide solution is prepared. Then 2.6 mL of H_2O_2 added in the solution. 0.25 g catalyst is added simultaneously with hydrogen peroxide and the experiment is run for 1 hour. At interval of 10 min, sample were taken, temperature and dissolved oxygen are recorded.

Experiment 4

Initial concentration = 600 ppm

Initial temperature = 26.4°C

Catalyst Loading = 0.25 g

Time (min)	Sulfide concentration (ppm)	Temperature (°C)	Dissolved oxygen (mg/L)
10	486	25.6	2.65
20	425	25.3	2.53
30	387	25.4	2.69
40	341	25.4	2.23
50	301	25.5	2.54
60	265	25.7	2.78

Table 4: Data recorded for initial sulfide concentration of 600 ppm

Experiment 5

Initial concentration = 800 ppm

Initial temperature = 24.5°C

Catalyst Loading = 0.25 g

Time (min)	Sulfide concentration (ppm)	Temperature (°C)	Dissolved oxygen (mg/L)
10	676	24.5	3.97
20	593	24.6	3.75
30	543	24.5	3.66
40	472	24.4	3.87
50	431	24.6	3.73
60	378	24.5	3.65

Table 5: Data recorded for initial sulfide concentration of 800 ppm

Experiment 6

Initial concentration = 1000 ppm

Initial temperature = 25.1°C

Catalyst Loading = 0.25 g

Time (min)	Sulfide concentration (ppm)	Temperature (°C)	Dissolved oxygen (mg/L)
10	892	25.1	2.36
20	751	25.1	2.37
30	701	25.2	2.48
40	651	25.1	2.21
50	543	25.3	2.34
60	492	25.2	2.26

Table 6: Data recorded for initial sulfide concentration of 1000 ppm

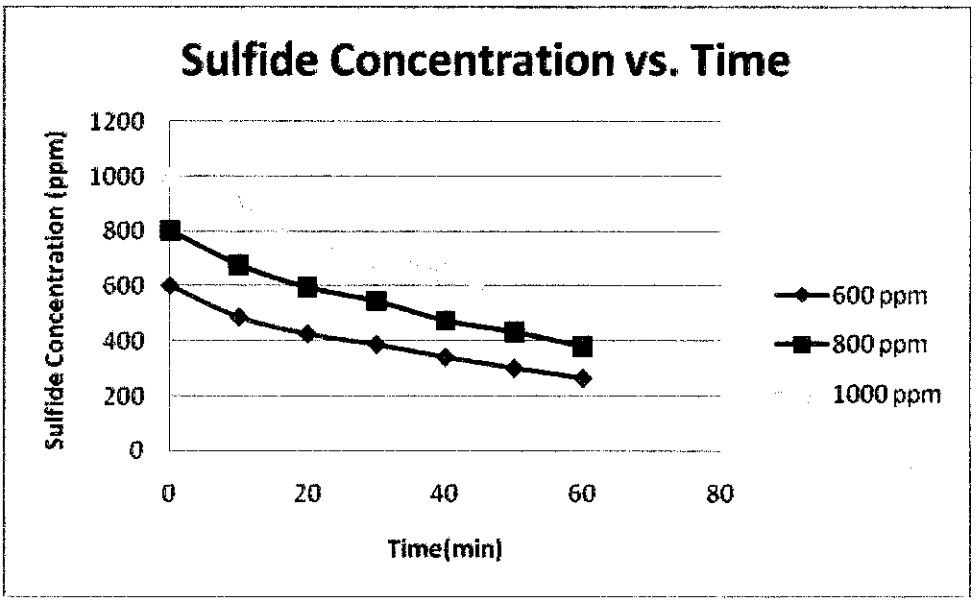


Figure 15: Sulfide Concentration vs. Time for different sulfide concentration parameter

The graph shows that sulfide concentration decrease evenly for all three variables. Higher sulfide concentration take longer time to convert to sulfate under constant hydrogen peroxide dosing, catalyst loading and temperature.

This experiment is done at room temperature. The dissolved oxygen is almost the same except for experiment 5 which is slightly higher. So the decrement per time is can be conclude almost the same. The lower initial sulfide concentration, less time will take for complete removal of sulfide.

CHAPTER 5
CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Removal of sulfides can be achieved by the catalytic process based on oxidation by hydrogen peroxide in the presence of hydrated ferric oxide as catalyst which was prepared in the laboratory. The characterization of the catalyst was done by SEM and FTIR. The catalyst particles were nearly uniform even though it hasn't reached the range of size required (1-200 nm). Almost complete removal can be achieved if the feed sulfide concentration is low or the catalyst loading is higher which in both ways the total oxidation of sulfide is higher. The results of this study are expected to be useful for any assessment or actual application in the industries.

5.2 RECOMMENDATION

The nature and the potential the nano-particles can still be discovered by further studies and more experiments in order to expand the usage and application of ferric oxide nano-particles.

One of the limitations while doing this project is the time constraint. The experiments can only be started on semester two, whereby in semester one the students only needed to do literature review. A lot of problem faced by students once they start the experiment such as no required chemicals in the laboratory, equipment broke down, or queuing for analysis done by technician. So, it is highly recommend for students to be allowed to start the experiment in semester one so they will have more time to complete their experiments.

Some of the equipments used in this experiment were giving wrong results. The maintenance and calibration of the equipment are not done regularly. If the maintenance of these equipments is taken care, it will help experiment process to run smoothly and to obtain more accurate results. Equipments like furnace which is highly used by students are limited. Only few of the furnaces in the lab are functioning. Most furnaces are broke down where it make the process late. Again, the laboratory equipments and also the analysis machine should be taken care. It is recommended the both maintenance and calibration should be done regularly to help students for completion of their respective experiments.

CHAPTER 6
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